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PFASs IN TAP VS. BOTTLED WATER: CO-OCCURRENCE, HEALTH RISKS AND REGULATORY GAPS

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Introduction

Per- and polyfluoroalkyl substances (PFASs) are globally recognized as persistent organic pollutants due to their resistance to degradation, bioaccumulative behavior, and potential to cause adverse health effects such as immune dysfunction, endocrine disruption, and cancer. These synthetic compounds are widely used in various consumer products and industrial processes, making them ubiquitous in environmental compartments. The increasing detection of PFASs in drinking water sources worldwide has raised urgent public health and regulatory concerns. In the European Union, new legislative frameworks such as Directive 2020/2184 have introduced monitoring requirements for 20 PFAS compounds, yet many emerging PFASs remain unregulated. Romania has aligned its national regulation through Ordinance 7/2023, but data regarding PFAS occurrence in drinking water sources, especially in bottled and tap water, remain scarce. Without such data, risk assessments and policy implementation remain limited.

This study aims to bridge this knowledge gap by applying advanced LC-MS/MS methods to evaluate the occurrence of both regulated and emerging PFASs in 45 drinking water samples collected across Romania. It further assesses co-occurrence patterns and performs a comprehensive human health risk assessment across multiple age and sex groups. The results provide critical input for shaping future regulatory decisions and public health protection strategies.

Materials and methods

Forty-five drinking water samples (24 tap and 21 bottled) were collected from various Romanian locations in PFAS-free polypropylene containers and analyzed within 48 hours. Target PFAS compounds, including both regulated and emerging substances, were extracted from 500 mL aliquots using Oasis® WAX solid-phase extraction cartridges, with isotopically labelled internal standards added for quantification. Analysis was performed using LC-MS/MS (Agilent 1260 LC coupled to 6410B triple quadrupole) in MRM mode, following chromatographic separation on a C18 column with ammonium acetate/methanol gradient. Method validation ensured recoveries between 90–110% and LOQs of 0.06 ng/L. A health risk

assessment was conducted by calculating estimated daily intake (EDI) and risk index (RI) values for various age and sex groups, using body weight and water consumption rates. Co-occurrence patterns were explored through Pearson correlation and principal component analysis (PCA).

Results and conclusions

The study revealed the widespread presence of both regulated and unregulated per- and polyfluoroalkyl substances (PFASs) in Romanian drinking water, with significant differences observed between tap and bottled water samples. Perfluorooctanoic acid (PFOA) was the most frequently detected compound, present in nearly all samples, with concentrations ranging from less than LOQ up to 17.2 ng/L in tap water and up to 4.48 ng/L in bottled water. Although all values remained below the EU parametric limit (100 ng/L for the sum of 20 PFASs), the frequent occurrence of multiple PFASs indicates chronic exposure risks, particularly through cumulative intake. Tap water showed overall higher PFAS burdens, with a mean total PFAS concentration of 10.8 ng/L compared to 5.34 ng/L in bottled water. Unregulated PFASs such as 4:2 fluorotelomer sulfonic acid (4:2 FTSA), hexafluoropropylene oxide dimer acid (HFPO-DA), GenX, and nonafluoro-3,6-dioxaheptanoic acid (NFDHA) were detected in over 50% of tap water samples, suggesting ongoing environmental contamination not yet covered by European regulations. PCA and Pearson correlation analyses indicated consistent co-occurrence patterns between regulated and unregulated compounds, implying common sources such as industrial discharge, surface water contamination, or degradation of precursor compounds. The human health risk assessment, based on EDI and RI, revealed that children are the most exposed population group, with RI values for PFOA exceeding 190—far above the safety threshold of 1. Other concerning compounds included perfluorooctane sulfonic acid (PFOS) and perfluorononanoic acid (PFNA), for which the risk indices in children also surpassed unity. While bottled water is commonly perceived as safer, some brands still showed detectable levels of PFOA and long-chain PFASs, challenging this assumption. Moreover, the simultaneous detection of multiple PFASs, even at low concentrations, raises concerns about potential additive or synergistic toxic effects. The elevated detection frequency of unregulated compounds, combined with their high persistence and poorly understood toxicity, underscores the need to revise monitoring frameworks. The results support the urgent extension of national legislation to include broader PFAS screening and call for increased transparency from bottled water producers and municipal suppliers regarding treatment processes.
This study provides the first comprehensive assessment of PFAS occurrence and health risk in Romanian drinking water. It highlights the urgent need for targeted policy updates, improved analytical monitoring, and risk communication to ensure the safety of both tap and bottled water.

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